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The Effect of Competing Ions on Copper Exchange by Clays

By R. P. Bush and L. E. Schultze

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

U.S. Department of the Interior
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Rhea L. Graham, Director

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

g	gram	mg	milligram
g/L	gram per liter	pct	percent
h	hour	°C	degree Celsius
meq	milliequivalent		

THE EFFECT OF COMPETING IONS ON COPPER EXCHANGE BY CLAYS

By R. P. Bush[1] and L. E. Schultze[2]

ABSTRACT

The U.S. Bureau of Mines performed Cu exchange capacity (CuEC) tests on Ca and Na montmorillonites and attapulgite clays. Mathematical models were developed from the data that the CuEC's are derived from for each clay as a function of pH, Cu concentration, and the concentrations of metal ions, which compete with Cu for exchange sites. An analysis was made of the impact of competing ions on Cu losses due to ion exchange. The results show that the CuEC's of clays, and hence Cu losses, are decreased by the presence of competing ions, and that Al and Mg have the largest impact of those cations normally present in Cu leaching solutions.

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INTRODUCTION

In an effort to develop a more environmentally acceptable alternative to open-pit mining for Cu, the U.S. Bureau of Mines (USBM) is investigating a novel mining technique known as in situ leaching. In this technique, leaching solution is injected into an ore body via wells that are sealed to the level of the ore body and solution containing dissolved Cu is pumped to the surface in a similarly sealed well. The solution can then be processed for recovery of Cu and recycled for further leaching. Injection wells are surrounded by recovery wells to minimize the amount of leaching solution that escapes the site.

One of the benefits of this method is that no waste rock needs to be moved or discarded, minimizing mining costs. Crushing, grinding, and transportation of ore, usually major costs in mining, are eliminated. Worker health and safety risks are reduced, as are labor costs in terms of personnel required. In situ mining is also more environmentally acceptable than open-pit mining because there is no surface disturbance and site reclamation is greatly facilitated (*1*).[3] Mining costs would include drilling and casing the wells, providing ground water monitoring both during operation and after site closure, and pumping solutions into and out of the site. After obtaining a pregnant Cu solution, Cu recovery costs would be comparable to conventional treatment at a Cu heap leaching operation where the Cu is recovered by solvent extraction and electrowinning.

There are drawbacks to the in situ method, however, including the uncertainty regarding solution recovery and adequate contact of solution with the minerals to be leached. Also, the ore deposit must be primarily an oxide so that it is amenable to in situ leaching, although research is underway to determine an appropriate in situ leaching process for sulfides.

An oxidized Cu ore body is highly altered and many gangue minerals will be present that are products of weathering or hydrothermal alteration. Some important examples of gangue minerals are clays, which are aluminosilicates having a layered structure, giving them a high-surface area. Cations that are adsorbed between the layers and on the surfaces as a result of natural weathering are readily exchanged with other cations in solutions that come into contact with the clay. As a result, any cations in a leaching solution that is in contact with clay will lead to cation exchange. This means that cations will attain equilibrium concentrations in the solution and on the clay, depending on the cation species present, their concentrations, and the clay minerals involved. This could lead to the loss of Cu in a pregnant leaching solution as it exchanges for other cations like Na and Ca. Other reactions may occur in which gangue minerals are broken down by acidic in situ leaching solutions, leading to a significant increase in the rate of natural weathering in the ore body. This may or may not be beneficial to leaching since cations other than Cu would be leached that could compete with Cu for exchange sites on the clay, but new clays would also be formed in the accelerated weathering process. Formation of new clays in fractures could lead to higher Cu losses due to ion exchange.

Each site will have different geological features, but as an example, the Santa Cruz site in New Mexico that the USBM's Twin Cities Research Center is using for an in situ leaching pilot study was examined. The Cu at this site occurs in two zones—an atacamite zone that contains mostly altered or secondary minerals but no clay and a chrysocolla zone that contains some disseminated clay. The disseminated clays are mostly kaolinite and some smectites, including Ca and Na montmorillonites. Clay in the fractures is mostly illite (*1*). Information from this borehole analysis illustrates the fact that there may be enough clay to cause some Cu losses as detailed in a previous report (*2*).

It is the purpose of this work to quantify the loss of Cu from a pregnant sulfuric acid leaching solution in the presence of the competing cations, which are expected to be present after a short period of leaching an oxidized Cu ore deposit in situ. This information was obtained through the use of an experimental design, which accounted for the expected range of concentrations of specific ions that were shown in previous USBM work to be of significance in clay ion exchange (*2*). The ions included in the study were Cu, Ca, Na, Mg, Al, Fe, K, Mn, Zn, and H. The model was used to describe the Cu exchange capacity (CuEC) of each clay in terms of each ion concentration and any interactions between them.

[3]Italic numbers in parentheses refer to items in the list of references at the end of this report.

MATERIALS AND PROCEDURES

The clays used in these experiments were as follows: Ca montmorillonite, Apache County, AZ; Na montmorillonite, Crook County, WY; and attapulgite, Gadsden County, FL. Samples of each clay were obtained from the National Clay Repository, Tuscaloosa, AL, and blended to ensure homogeneity. These clay samples were used because they are the most pure, representative, and homogeneous samples of each clay available. Elemental analyses of the clays are shown in table 1, and each sample was approximately 80 pct passing 200 mesh as received. Previous USBM work indicated that kaolinite and ripidolite were not significant Cu exchangers, so they were not included in this study (*2*). After finding that the CuEC of attapulgite in the presence of competing ions was very low, illite was also eliminated from consideration since prior USBM work showed it had a lower CuEC than attapulgite (*2*). Solutions were prepared using reagent-grade sulfate salts and distilled water. The pH of each test solution was adjusted with sulfuric acid.

Table 1.—Typical analyses of clay minerals, weight percent

Element	Ca montmorillonite	Na montmorillonite	Attapulgite
Al	7.9	9.5	4.8
Ca	1.7	1.0	1.1
Cu	.012	.009	.008
Fe	.97	2.7	2.2
K	.22	0.21	.23
Mg	3.3	1.5	5.3
Mn	.095	.011	.024
Na	.11	.84	.063
P	<.1	<.1	.38
Si	26.5	30.0	27.9
Ti	.13	.070	.28
Zn	.12	.077	.017

Tests were done in screw-top Erlenmeyer flasks placed in a shaking water bath at constant temperature. All tests were conducted at 25 °C because previous USBM work showed that temperature had little effect on exchange capacity (*2*). A contact time of 1 h was selected since earlier work showed that essentially all exchange was complete in 1 h (*2*). Experiments were performed to determine CuEC's for the three clays using a face-centered cube statistical design as outlined in the study by Rautela (*3*). Mathematical models were developed that describe the CuEC's for each clay within the concentration ranges used. The ionic species and concentrations used were based on gangue mineral compositions and reactions that are expected to occur during the course of in situ leaching of an oxide Cu ore using sulfuric acid (*4-7*).

Clay samples were added to solutions containing the test ions. Concentrations of Cu, Al, Na, Ca, Mg, Fe, Mn, Zn, K, and pH in the initial solutions were selected to yield an equilibrium concentration matching the preselected design. None of the tests included all of these ion species. Tests were repeated until equilibrium values were within 10 pct of the desired value. All tests were run in triplicate to increase precision of the results. Cation CuEC's were calculated based on the change in Cu concentrations after clay contact. The resulting data were analyzed using a multiple-regression analysis, and tests yielding data having residuals greater than two standard deviations were repeated to verify the results. It must be kept in mind that the resulting regressed equations are only valid over the range of concentrations included in the tests.

Contour plots were prepared using the regressed equations by holding all but two of the variables constant while allowing Cu concentration and one other variable to vary over the test range at values of constant CuEC. These plots illustrate the effect of each variable compared with the effect of Cu concentration on the resulting CuEC for each clay studied.

RESULTS AND DISCUSSION

The concentrations for each ion were evenly spaced over the design range to simplify regression analysis yielding normalized values of -1, 0, and 1. A mathematical model was subsequently developed, including combinations of each variable having a significant contribution to the observed response. These combinations included each ion concentration, each ion concentration squared to account for curvature, and each ion concentration paired with each other one to account for interactions between ion concentration effects. For example, in the test of attapulgite CuEC, the variables tested included H, Cu, and Mg concentrations. The resulting variables tested for significance included pH, pH^2, Cu, Cu^2, Mg, Mg^2, pH-Cu, pH-Mg, and Cu-Mg. A statistical package was used to determine significance of each variable as it was entered into the equation by applying the Student's t-test at the 0.05 level. This means that only those terms having less than a 5-pct probability of arising from random error were included. If the resulting equation exhibited an adjusted coefficient of correlation of 0.95 (adjusted to account for the number of degrees of freedom in the data set), there is a 95-pct probability that a measured data point will be described by the equation. The equation can then be used by entering values for each ion in grams per liter or pH units to determine CuEC in milliequivalents per 100 g of clay, a standard method of reporting clay ion exchange capacity.

Ca MONTMORILLONITE

The CuEC of Ca montmorillonite was determined using the conditions shown in table 2, with Cu ranging from 0.5 to 2.5 g/L, Ca from 0.4 to 0.6 g/L, Mg from 0.5 to 3.5 g/L, and pH from 1 to 3. This resulted in 25 condition sets. The first 16 sets of conditions shown in table 2 represent the corners of a four-dimensional cube, containing high and low values. The next eight sets represent the faces, and the last represents the center, each containing medium values. The mathematical model developed using the statistical package yielded an equation with an adjusted coefficient of correlation of 0.99. The equation for CuEC in milliequivalents per 100 g clay for Ca montmorillonite is as follows:

$$\begin{aligned} CuEC = {} & 16.5Cu - 6.87Mg + 1.6(Mg)^2 \\ & - 2.84(Cu)(Mg) - 0.746(Mg)(pH) \\ & + 10.8pH - 1.98(pH)^2 - 0.851. \end{aligned} \quad (1)$$

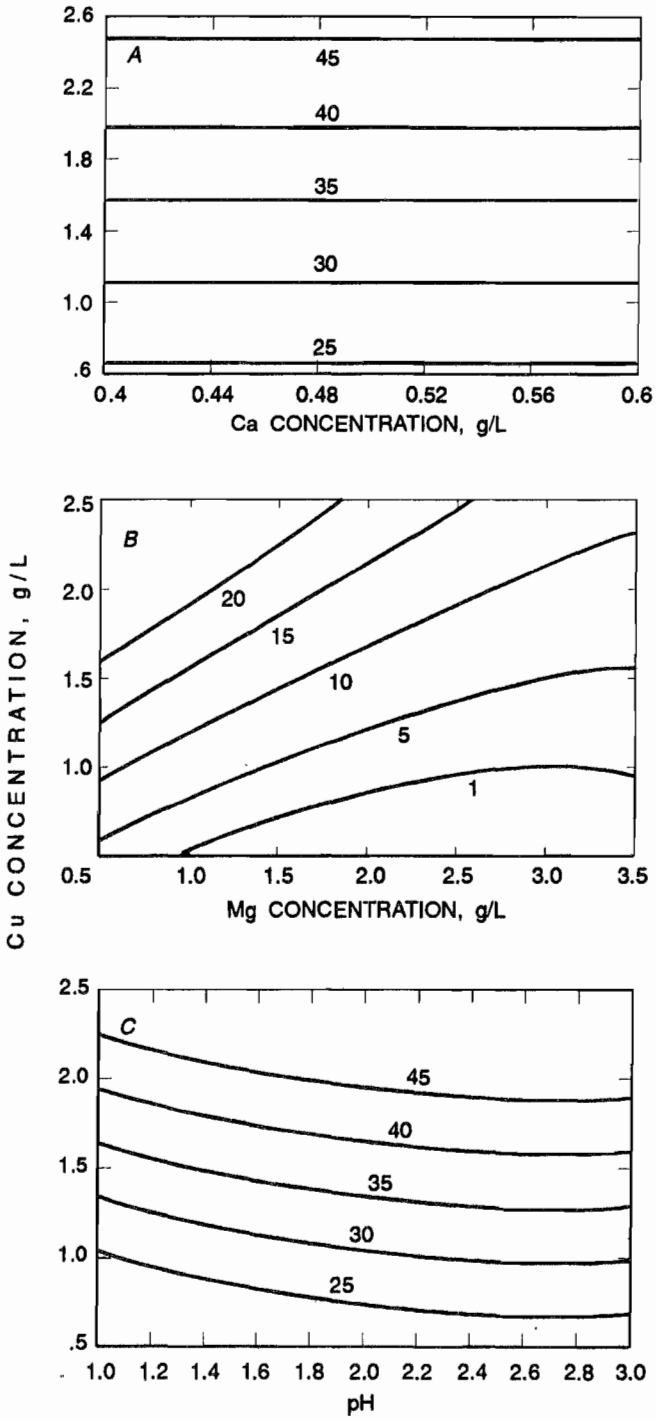
The negative Ng coefficient indicates that Mg competes effectively with Cu. Inspection of the data in table 2 reveals that in each case where CuEC exceeds 40 meq per 100 g, Cu is at its high level while Mg is at its low level. For those cases where Mg is high and Cu is low, CuEC is less than 5 meq per 100 g. Both high and low CuEC can be found over the entire range of pH. A term for Ca was not included in equation 1 since Ca concentration did not have a statistically significant effect on the CuEC of Ca montmorillonite.

Figure 1*A* is a contour plot of CuEC as a function of Cu and Ca at 0.5 g/L Mg and pH 3. The plot shows that Ca has no effect on CuEC for Ca montmorillonite. Figure 1*B* is a plot of CuEC as a function of Cu and Mg at 0.4 g/L Ca and pH 3. Increasing Mg concentration decreases CuEC significantly. Figure 1*C* is a contour plot of CuEC as a function of Cu and pH at 0.4 g/L Ca and 0.5 g/L Mg. The plot shows that increasing pH has a small positive effect on CuEC.

Table 2.—Test conditions and CuEC's for Ca montmorillonite

Condition set	Concentration, g/L			pH	CuEC observed, meq per 100 g clay
	Ca	Cu	Mg		
1	0.4	0.5	0.5	1	11.8
2	.6	.5	.5	1	11.7
3	.4	2.5	.5	1	40.1
4	.6	2.5	.5	1	44.2
5	.4	.5	3.5	1	4.1
6	.6	.5	3.5	1	4.5
7	.4	2.5	3.5	1	19.6
8	.6	2.5	3.5	1	15.2
9	.4	.5	.5	3	17.6
10	.6	.5	.5	3	17.1
11	.4	2.5	.5	3	48.9
12	.6	2.5	.5	3	45.2
13	.4	.5	3.5	3	5.4
14	.6	.5	3.5	3	4.9
15	.4	2.5	3.5	3	17.1
16	.6	2.5	3.5	3	19.1
17	.5	1.5	2.0	2	17.3
18	.5	1.5	2.0	2	17.1
19	.5	.5	2.0	2	8.5
20	.5	2.5	2.0	2	30.5
21	.5	1.5	.5	2	32.1
22	.5	1.5	3.5	2	12.0
23	.5	1.5	2.0	1	16.0
24	.5	1.5	2.0	3	16.9
25	.5	1.5	2.0	2	20.8

Figure 1



Contour plots of CuEC as functions of Cu, Ca, Mg, and pH for Ca montmorillonite. A, At 0.5 g/L Mg and pH 3; B, at 0.4 g/L Ca and pH 3; C, at 0.4 g/L Ca and 0.5 g/L Mg. Contours are constant CuEC's that were calculated from equation 1 in milliequivalents per 100 g clay.

Na MONTMORILLONITE

The CuEC of Na montmorillonite was determined using the conditions shown in table 3, with Cu ranging from 0.5 to 2.5 g/L, Na from 0.3 to 0.9 g/L, Ca from 0.4 to 0.6 g/L, Mg from 0.5 to 3.5 g/L, and pH from 1 to 3. Using the experimental design as outlined above, 27 different sets of conditions were tested. The sets of experimental conditions listed in table 3 are in a face-centered cube arrangement. For Na montmorillonite, having 5 variables, the first 16 condition sets represent the corners of a five-dimensional cube, containing high and low values. The next 10 sets represent the faces, and the last set represents the center of the cube, containing medium-level values. The CuEC in units of milliequivalents per 100 g clay for Na montmorillonite can be calculated from the following equation:

$$\begin{aligned} CuEC = {} & 9.93Cu - 12.9(Ca)^2 \\ & - 5.69Mg + 1.21(Mg)^2 - 2.10(Cu)(Mg) \\ & - 1.20(pH)(Mg) + 4.32pH + 1.36 \\ & + 5.17(Ca)(Mg) - 2.28(Ca)(Na). \end{aligned} \quad (2)$$

Table 3.—Test conditions and CuEC's for Na montmorillonite

Condition set	Concentration, g/L				pH	CuEC observed, meq per 100 g clay
	Ca	Cu	Mg	Na		
1	0.4	0.5	0.5	0.3	3	10.5
2	.6	.5	.5	.3	1	3.8
3	.4	2.5	.5	.3	1	22.0
4	.6	2.5	.5	.3	3	28.4
5	.4	.5	3.5	.3	1	2.5
6	.6	.5	3.5	.3	3	3.4
7	.4	2.5	3.5	.3	3	8.2
8	.6	2.5	3.5	.3	1	9.3
9	.4	.5	.5	.9	1	5.5
10	.6	.5	.5	.9	3	9.3
11	.4	2.5	.5	.9	3	31.5
12	.6	2.5	.5	.9	1	18.8
13	.4	.5	3.5	.9	3	2.1
14	.6	.5	3.5	.9	1	1.7
15	.4	2.5	3.5	.9	1	6.4
16	.6	2.5	3.5	.9	3	6.9
17	.4	1.5	2.0	.6	2	7.3
18	.6	1.5	2.0	.6	2	8.1
19	.5	.5	2.0	.6	2	14.0
20	.5	2.5	2.0	.6	2	3.8
21	.5	1.5	.5	.6	2	21.6
22	.5	1.5	3.5	.6	2	7.9
23	.5	1.5	2.0	.3	2	9.3
24	.5	1.5	2.0	.9	2	8.0
25	.5	1.5	2.0	.6	1	10.7
26	.5	1.5	2.0	.6	3	6.6
27	.5	1.5	2.0	.6	2	8.3

The effect of Mg is difficult to determine from equation 2 because of the number of terms to which it contributes. Inspection of the data in table 3 reveals that in none of the cases where Mg exceeds its minimum level, does CuEC exceed 20 meq per 100 g, demonstrating successful competition with Cu for exchange sites. Competition by Ca and H is less effective since high CuEC values are found at both high and low values for the respective cations.

The effects of each ion can be seen more clearly in figure 2. The contours in figure 2*A* represent CuEC as a function of Mg and Cu concentrations at 0.4 g/L Ca, 0.3 g/L Na, and pH 3. As Mg concentration increases across the figure from left to right, progressively lower Cu exchange profiles are crossed. This shows that increasing Mg concentration effectively decreases CuEC. Figure 2*B* is a plot of CuEC contours as a function of Ca and Cu concentrations at 0.5 g/L Mg, 0.3 g/L Na, and 0.3 g/L Na. This shows that Ca has little effect on CuEC since all contours are nearly parallel to the Ca axis. Figure 2*C* shows CuEC contours as a function of pH and Cu concentration at 0.4 g/L Ca, 0.5 g/L Mg, and 0.3 g/L Na. Increasing pH does cause an increase in CuEC at all Cu concentrations studied.

ATTAPULGITE

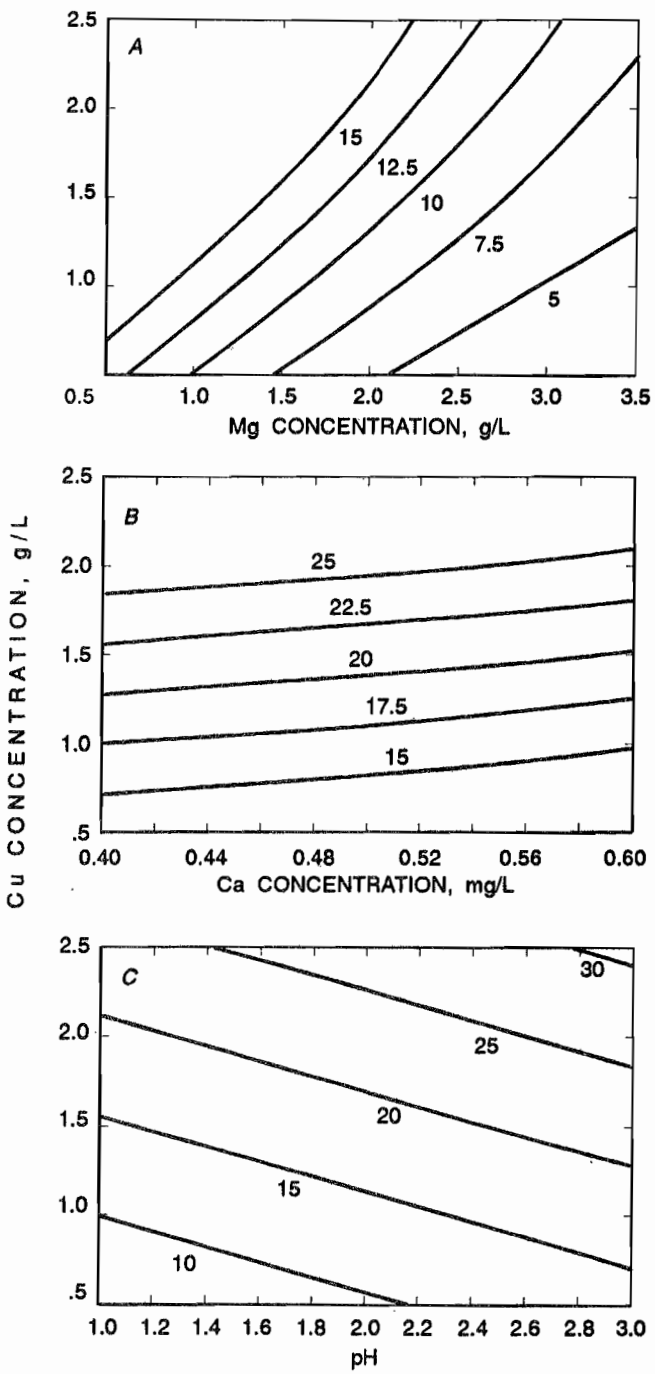
The last clay included in this study was attapulgite. Test conditions were as follows: 0.5 to 2.5 g/L Cu, 0.5 to 3.5 g/L Mg, and pH 1 to 3. This resulted in a series of 15 sets of conditions as shown in table 4. The first eight sets of conditions shown in table 4 represent the corners of a three-dimensional cube, containing high and low values. The next six sets represent the faces, and the last represents the center, each containing medium values. The developed equation has an adjusted coefficient of correlation of 0.89. The CuEC for attapulgite in milliequivalents per 100 g of clay can be estimated from the following equation:

$$CuEC = 1.26Cu + 1.22pH + 1.15Mg + 1.06(pH)(Cu) - 0.58(Cu)(Mg) - 0.54(pH)(Mg) - 2.32. \quad (3)$$

Because of the much lower CuEC's measured for the attapulgite as compared with those measured for the montmorillonites, the effects of cation competitions are less obvious. Both high and low CuEC's are observed for the high pH.

Figure 3 shows more clearly the effects of pH and Mg ion concentration on CuEC values. Figure 3*A* is a contour

Figure 2



Contour plots of CuEC as functions of Cu, Mg, Ca, and pH for Na montmorillonite. A, At 0.4 g/L Ca, 0.3 g/L Na, and pH 3; B, at 0.5 g/L Mg, 0.3 g/L Na, and pH 3; C, at 0.4 g/L Ca, 0.5 g/L Mg, and 0.3 g/L Na. Contours are constant CuEC's that were calculated from equation 2 in milliequivalents per 100 g clay.

plot of CuEC as a function of Cu and pH at 0.5 g/L Mg. This figure indicates that pH has a positive effect on CuEC. Figure 3*B* is a contour plot of CuEC as a function of Cu and Mg at pH 3. This figure shows that Mg has a negative effect on CuEC.

Table 4.—Test conditions and CuEC's for attapulgite

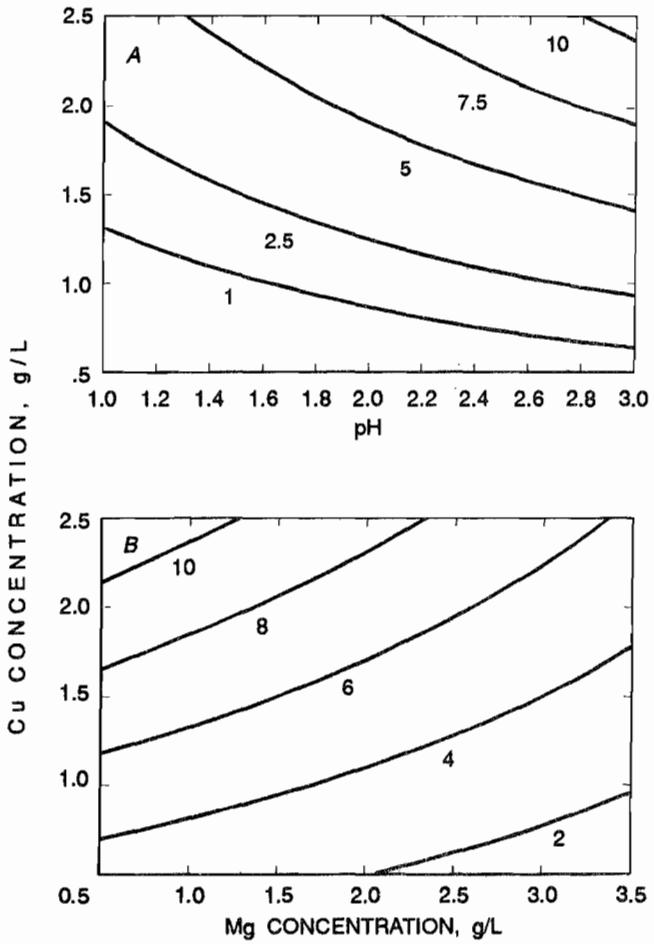
Condition set	Concentration, g/L		pH	CuEC observed, meq per 100 g clay
	Cu	Mg		
1	0.5	0.5	1	0.6
2	2.5	.5	1	4.0
3	.5	.5	1	.6
4	2.5	3.5	1	2.2
5	.5	.5	3	3.3
6	2.5	.5	3	12.6
7	.5	3.5	3	1.7
8	2.5	3.5	3	5.9
9	.5	2.0	2	1.6
10	2.5	2.0	2	5.4
11	1.5	.5	2	3.8
12	1.5	3.5	2	1.9
13	1.5	2.0	1	2.5
14	1.5	2.0	3	3.7
15	1.5	2.0	2	4.1

OTHER COMPETING IONS

Since several ions other than Ca, Mg, and Na are known to be present in actual Cu leaching solutions, tests were done to include these ions and to expand the range of the previous tests. Analyses of solutions from several Cu companies resulted in the following maximum concentrations of metals, in grams per liter, to be used in further tests: Al, 13; Fe, 4.4; Mg, 12; Mn, 3; K, 1; and Zn, 2. A series of screening tests were run, comparing each of these metals as competitors with Cu, both singly and in pairs to determine which were significant. Sodium montmorillonite was chosen since it exhibited high CuEC in the absence of competing ions. Equilibrium Cu concentration was held constant at 2.5 g/L and pH was held constant at 3, conditions yielding maximum CuEC in previous tests.

The measured CuEC, as shown in table 5, demonstrates which ions effectively compete with Cu. The Al, while at a much higher concentration than the Cu, is the strongest competitor for exchange sites as evidenced by the low CuEC in its presence. Potassium is a poor competitor since its addition resulted in the smallest decrease in CuEC. Iron, magnesium, and zinc all decrease CuEC, but to a lesser extent than Al and Mg. Magnesium competes almost as strongly as Al as evidenced by the test results that showed that CuEC was lowered to 3.2 meq per 100 g by the addition of 12 g/L Mg. Similarly, additions of Fe, Mn, K, or Zn in conjunction with Al result in only small differences in CuEC.

Figure 3



Contour plots of CuEC as functions of Cu, Mg, and pH for attapulgite. A, At 0.5 g/L Mg; B, at pH 3. Contours are constant CuEC's that were calculated from equation 3 in milliequivalents per 100 g clay.

Another test matrix was set up with Ca montmorillonite, including 0.5 to 14.5 g/L Al, 0.5 to 6.5 g/L Cu, 0.5 to 12.5 g/L Mg, and pH 1 to 3. The test matrix used and the measured responses are shown in table 6. The first 16 sets of conditions shown in table 6 represent the corners of a four-dimensional cube, containing high and low values. The next eight sets represent the faces, and the last represents the center, each containing medium values.

Table 5.—Comparison of effect of potential competing ions on CuEC's for Na montmorillonite

Condition set	Concentration, g/L						CuEC observed, meq per 100 g clay
	Al	Fe	K	Mg	Mn	Zn	
1	0	0	0	0	0	0	42.4
2	0	0	1	0	0	0	32.8
3	0	0	0	0	0	2.5	17.0
4	0	5	0	0	0	0	13.2
5	0	0	0	0	3.5	0	12.2
6	0	0	0	3.5	0	0	9.6
7	0	5	0	3.5	0	0	8.8
8	0	0	0	12	0	0	3.2
9	15	0	0	3.5	0	0	2.8
10	15	0	1	0	0	0	1.1
11	15	0	0	0	0	2.5	0.3
12	15	0	0	0	3.5	0	0.1
13	15	0	0	0	0	0	0
14	15	5	0	0	0	0	0

Table 6.—Test conditions and CuEC's for Ca montmorillonite with Al, Cu, and Mg

Condition set	Concentration, g/L			pH	CuEC observed, meq per 100 g clay
	Al	Cu	Mg		
1	0.5	0.5	0.5	1	4.6
2	14.5	.5	.5	1	.7
3	.5	6.5	.5	1	36.0
4	14.5	6.5	.5	1	5.2
5	.5	.5	12.5	1	1.2
6	14.5	.5	12.5	1	.7
7	.5	6.5	12.5	1	9.5
8	14.5	6.5	12.5	3	3.3
9	.5	.5	.5	3	6.4
10	14.5	.5	.5	3	1.4
11	.5	6.5	.5	3	43.1
12	14.5	6.5	.5	3	6.0
13	.5	.5	12.5	3	1.8
14	14.5	.5	12.5	3	1.2
15	.5	6.5	12.5	3	13.4
16	14.5	6.5	12.5	3	5.4
17	.5	3.5	6.5	2	9.8
18	14.5	3.5	6.5	2	2.6
19	7.5	.5	6.5	2	1.6
20	7.5	6.5	6.5	2	7.8
21	7.5	3.5	.5	2	5.9
22	7.5	3.5	12.5	2	3.3
23	7.5	3.5	6.5	1	3.5
24	7.5	3.5	6.5	3	4.7
25	7.5	3.5	6.5	2	6.0

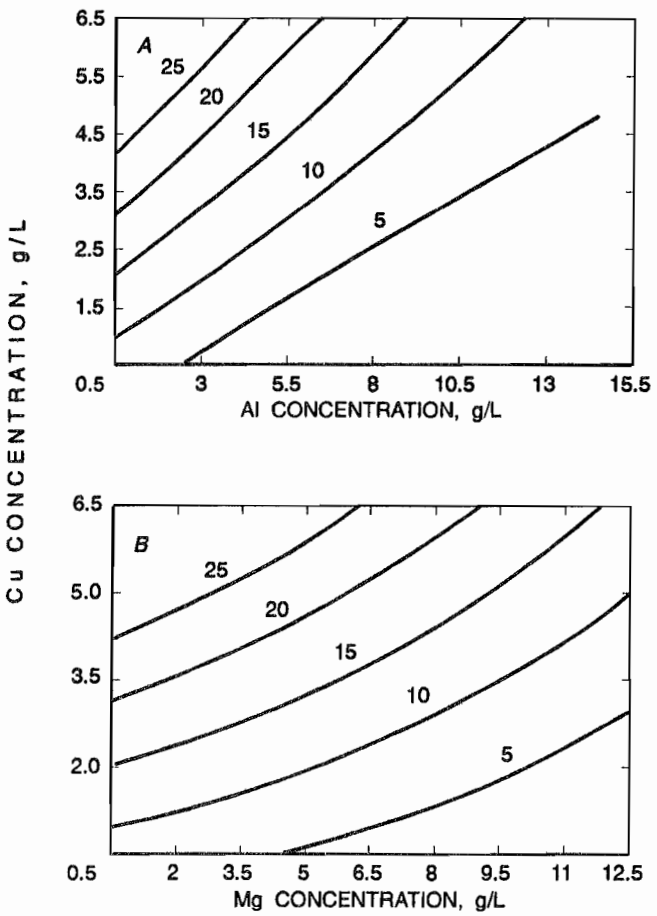
The CuEC in milliequivalents per 100 g of clay for Ca montmorillonite can be estimated with the following equation:

$$CuEC = 6.81 + 4.79Cu - 1.79Al - 0.72Mg - 0.21(Al)(Cu) + 0.09(Al)(Mg) - 0.18(Cu)(Mg) + 0.08(Al)^2. \quad (4)$$

Equation 4 fits the data with an adjusted coefficient of correlation of 0.88. There is no term for pH, demonstrating that strongly adsorbed ions such as Al and Mg overwhelm any contribution from H^+. Inspection of the data in table 6 reveals that CuEC never exceeds 6 meq per 100 g when Al is at its highest level, demonstrating its ability to compete with Cu for available exchange sites. Magnesium is a less effective competitor in the presence of Al since values as high as 13.4 meq per 100 g were observed, even at high addition levels.

Figure 4 graphically shows the effect of Al and Mg on CuEC. Figure 4*A* is a contour plot of CuEC as a function of Cu and Al at 0.5 g/L Mg and pH 3. The plot shows that increasing Al concentration has a negative impact on CuEC values. Figure 4*B* is a contour plot of CuEC as a function of Cu and Mg at 0.5 g/L Al and pH 3. It

Figure 4



Contour plots of CuEC as functions of Cu, Al, and Mg. A, At 0.5 g/L Mg and pH 3; B, at 0.5 g/L Al and pH 3. Contours are constant CuEC's that were calculated from equation 4 in milliequivalents per 100 g clay.

demonstrates a negative impact on CuEC with increasing Mg concentration.

IMPACT OF ION EXCHANGE ON Cu RECOVERY

Equations 1 through 4 developed for CuEC can be used to predict the impact of ion CuEC on Cu recovery during in situ leaching. Cu losses can be calculated based on Cu and clay content of the ore, leaching solution composition, and clay type. A similar calculation was done in previous USBM work (*2*) to demonstrate possible Cu losses and is redone here to include the effect of competing ions. To make direct comparisons, CuEC was calculated using the appropriate equations, Cu concentration of 1.8 g/L, and pH 2.5 (table 7). The results demonstrate that the presence of as little as 0.5 g/L of a strongly competing ion such as Mg can decrease Cu losses by as much as 42 pct. When the concentration of Mg or Mg plus Al exceeds that of the Cu, losses are reduced to less than 25 pct.

Table 7.—Impact of competing ions on clay CuEC and Cu recovery[1]

Condition set	Competing ion, g/L			CuEC, meq per 100 g clay	Cu loss per 100 g ore, mg	Cu loss, pct
	Al	Ca	Mg			
Ca MONTMORILLONITE						
1	0	0	0	65	200	100
2	0	0	0.5	37	120	58
3	0.5	0	.5	14	44	22
4	0	0	3.5	15	47	23
5	14.5	0	12.5	4.1	13	6.5
Na MONTMORILLONITE						
1	0	0	0	42	130	67
2	0	0.4	0.5	22.8	72.4	36.2
3	0	.6	3.5	0	0	0
ATTAPULGITE						
1	0	0	0	9.5	30	15
2	0	0	0.5	7.1	22.7	11.4
3	0	0	3.5	3.4	10.8	5.4

[1]Test conditions: 1.8 g/L Cu; pH 2.5; ore containing 0.2 pct Cu, 10 pct clay; 100 pct Cu leached from ore.

CONCLUSIONS

Previous USBM work indicated that Cu losses due to ion exchange could be significant when leaching an oxidized Cu ore in situ (*2*). While this is true for solutions containing only Cu, the present work demonstrates that solutions containing other ions, especially Al and Mg, will lose less soluble Cu to clay in the ore. These test results indicate that Al and Mg have the most significant impact on exchange capacity for the clays studied. Calcium, iron, manganese, potassium, sodium, and zinc have little, if any, impact on CuEC.

The CuEC of each clay varied as before, with Ca montmorillonite having the highest capacity, followed by Na montmorillonite and attapulgite. Illite, ripidolite, and kaolinite were not tested, since they were shown to have a low capacity in solutions containing only Cu. Once again, equations 1 through 4 can only be used for estimating CuEC's over the range of concentrations used for each ion.

Aluminum, magnesium, and other cations will be leached from the gangue minerals when sulfuric acid is applied in the in situ leaching operation. The impact of ion exchange by clays on Cu recovery will thus be decreased naturally by the ore as it is leached.

REFERENCES

1. U.S. Bureau of Mines. In Situ Leach Mining. IC 9216, 1989, pp. 2-3.

2. Gomer, J. S., S. W. Yopps, S. P. Sandoval, and A. E. Clark. Copper Exchange Capacity of Clays and Their Potential Effect on In Situ Copper Leaching. USBM RI 9396, 1992, 10 pp.

3. Rautela, G. S., R. D. Snee, and W. K. Miller. Response-Surface Co-Optimization of Reaction Conditions in Clinical Chemical Methods. Clin. Chem. (Winston-Salem, NC), v. 25, No. 11, 1979, pp. 1954-1964.

4. Ahlness, J. K., and M. G. Pojar. In Situ Copper Leaching in the United States: Case Histories of Operations. USBM IC 8961, 1983, 37 pp.

5. Sheffer, H. W., and L. G. Evans. Copper Leaching Practices in the Western United States. USBM IC 8341, 1968, 57 pp.

6. Longwell, R. L. In Place Leaching of a Mixed Copper Ore Body. Paper in Proceedings of Solution Mining Symposium 1974, ed. by F. F. Aplan, W. A. McKinney, and A. D. Pernichele. AIME, 1974, pp. 233-242.

7. Bampton, K. F., F. Bologiannis, J. H. Canterford, and A. N. Smith. Development of Experimental In Situ Leaching at the Mutooroo Copper Mine, South Australia. Paper in the Australian Institute of Mining and Metallurgy Broken Hill Conference. Aust. Inst. Min. Metall., v. 12, 1983, pp. 371-379.